





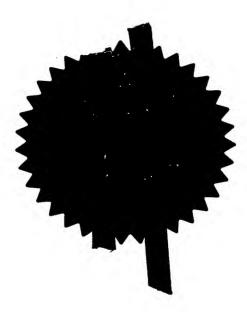
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Dated 11 February 2003

An Executive Agency of the Department of Trade and Industry

# METHOD AND SUBSTRATE FOR THE PREPARATION OF A PRINTING PLATE

#### FIELD OF THE INVENTION

This invention relates to a method and substrate for the preparation of a printing plate suitable for lithographic printing.

#### BACKGROUND OF THE INVENTION

Printing plates suitable for offset lithographic printing are known which comprise a support having non-image areas which are hydrophilic and image areas which are hydrophobic and ink-receptive.

The art of lithographic printing is based upon the immiscibility of oil and water, wherein the oily material or ink is preferentially retained by the image area and water or fountain solution is preferentially retained by the non-image area. When a suitably prepared surface is moistened with water and an ink is then applied the background or non-image area retains the water and repels the ink while the image area accepts the ink and repels the water. The ink on the image area is then transferred to the surface of a material upon which the image is to be reproduced, such as paper, cloth and the like.

Commonly the ink is transferred to an intermediate material called the blanket which in turn transfers the ink to the surface of the material uponwhich the image is to be reproduced.

Inkjetting is the non-impact method for producing images by the deposition of ink droplets on a substrate in response to digital signals.

JP-A-53015905 describes the preparation of a printing plate by inkjetting an alcohol-soluble resin in an organic solvent onto an aluminum printing plate.

JP-A-56105960 describes the formation of a printing plate by inkjetting onto a support e.g. an anodised aluminum plate an ink capable of forming an oleophilic image and containing a hardening substance such as epoxysoybean oil together with benzoyl peroxide or a photo-hardening substance such as an unsaturated polyester.

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EP-A-0 882 584 describes a method of preparing a printing plate comprising producing an oleophilic image on the surface of a support by inkjet printing the image on the surface using an aqueous solution or of a salt of a hydrophobic organic acid e.g. oleic acid.

U.S. Patent No. 6131514 describes a method of preparing a printing plate comprising producing an oleophilic image on the surface of a support by inkjet printing the image on the surface using an aqueous solution or aqueous colloidal dispersion of a polymer bearing water-solubilising groups wherein the water solubilising groups interact with the surface of the support thereby binding the polymer to the support and rendering the polymer insoluble.

### PROBLEM TO BE SOLVED

Inkjet printing provides a rapid and simple way of preparing a printing plate directly from digital information on a computer which uses simpler and much less expensive equipment than commonly used computer-to-plate systems, which use high power lasers in the case of thermal effect platesetters, or lower power lasers together with a wet processing step in the case of visible light platesetters.

It is preferred that the inkjet writing fluids are water-based for environmental and health reasons, and also to avoid the excessive evaporation and drying out at the jets which can occur with moderately volatile organic solvents.

However, known methods of preparing lithographic printing plates by applying aqueous solutions of oleophilising agent by inkjet only give good results when grained anodised aluminium is used as the printing plate substrate, and for some applications it is desired to use a substrate such as polyester film or a paper substrate which is less expensive, lighter in weight, and easier to transport through an inkjet printer than aluminium. The present invention enables this.

It is also found that some oleophilising agents when used with grained anodised aluminium as the printing plate substrate show improved performance on the press when the aluminium substrate is coated with a hydrophilic layer according to the invention.

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#### SUMMARY OF THE INVENTION

The invention provides a method for the preparation of a printing plate comprising forming an oleophilic image on a substrate for a printing plate comprising a support having a hydrophilic layer on its surface, the oleophilic image being formed by inkjet printing an aqueous solution or aqueous colloidal dispersion of an anionic oleophilising agent on the surface of the support and drying the applied solution or dispersion, such that on drying the area of the surface to which the solution or dispersion was applied becomes lithographic inkaccepting, characterised in that the hydrophilic layer comprises a crosslinked cationic polymer.

The invention also provides a substrate for a printing plate comprising a support having a hydrophilic layer on its surface wherein the hydrophilic layer comprises a crosslinked cationic polymer.

#### DETAILED DESCRIPTION OF THE INVENTION

The support for the substrate of the invention may be any material having suitable thickness and mechanical properties for use as a printing plate on a lithographic printing press. Suitable supports include metallic, polymeric and paper-based supports e.g. sheets or foils. Specific examples of supports include sheet aluminium, which may be grained and anodised, polyester film and supports which comprise fibrous material bound together with suitable resin or polymer.

The support is coated with a layer comprising a cationic polymer, that is a polymer which bears positively charged groups attached to the polymer chain. Preferably the polymer bears primary, secondary, tertiary or quaternary amino groups.

Examples of suitable cationic polymers include polyalkylenepolyamines and alkylated derivatives thereof, products of addition of alkylcarboxylic acids and polyalkylenepolyamines, products of addition of ketones and polyalkylenepolyamines, products of addition of aldehydes and polyalkylenepolyamines, products of addition of isocyanates and polyalkylenepolyamines, products of addition of isothiocyanates and polyalkylenepolyamines, products of addition of alkylene oxides and

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polyalkylenepolyamines, and products of addition of polyalkylene oxide block copolymers and polyalkylenepolyamines.

A particularly preferred polymer is polyethyleneimine.

The polymer may be applied to the support as an aqueous solution, and the pH of the solution may be adjusted to a value from pH 3 to pH 10, preferably from pH 5 to pH 9.

The cationic polymer may be present in an amount from 0.01 to  $10 \text{ g/m}^2$ , preferably from 0.05 to 1.0 g/m<sup>2</sup>.

Other compatible polymers, such as polyvinyl alcohol or polyvinylpyrrolidone, may be present in addition to the cationic polymer.

The coated layer is crosslinked with a suitable crosslinking agent to render it insoluble in water and of sufficient mechanical strength.

Examples of crosslinking agents which react with amino groups, include formaldehyde, dialdehydes such as gluteraldehyde and succinaldehyde, epoxy compounds, and activated vinyl compounds such as bis (vinyl sulphonyl) methane, and bis (vinyl sulphonyl methyl) ether.

Further examples of crosslinking agents are described in chapter 2 of "The Theory of the Photographic Process", Fourth Edition, edited by T. H. James and published by the Eastman Kodak Company, 1977.

The amount of crosslinking agent employed may be from 1 to 100 w/w%, preferably from 3 to 30 w/w%, based on the weight of the cationic - polymer.

Inorganic particulate materials, such as silica, alumina, titanium dioxide or kaolin may be incorporated in the coated hydrophilic layer.

The inorganic particulate material may be present in an amount from 0.1 to  $30 \text{ g/m}^2$ , preferably from 0.5 to  $10 \text{ g/m}^2$ .

Additional layers may be coated above or below the cationic polymer layer, including adhesion-promoting layers such as gelatin between the cationic polymer layer and the support. Preferably, the cationic polymer layer is the outermost layer.

The writing fluid comprises an aqueous solution or colloidal dispersion of an anionic oleophilising agent. In one aspect of the invention, the

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aqueous solution or colloidal dispersion of the anionic oleophilising agent does not comprise pigment particles dispersed therein.

Preferably, the anionic oleophilising agent is a hydrophobic organic acid or a salt thereof. The hydrophobic organic acid may be selected from hydrophobic organic carboxylates, sulphonates, sulphates, phosphonates and phosphates. Examples of suitable hydrophobic organic acids or salts thereof include fatty acids and their salts. The hydrophobic organic acid or salt thereof may be an anionic surfactant.

Examples of monobasic carboxylic and sulphonic acids with hydrophobic groups which function as oleophilising agents are given in EP-A- 882 584, and include oleic acid, stearic acid and surfactants such as AEROSOL® TR70.

Examples of monobasic phosphoric and phosphonic acids with hydrophobic groups which function as oleophilising agents are given in EP-A- 1 157 825.

Examples of dibasic carboxylic acids and dibasic sulphoniccarboxylic acids with hydrophobic groups which function as oleophilising agents are given in our copending simultaneously filed GB patent application entitled "Method for the Preparation of a Printing Plate" (Docket 84108).

The hydrophobic organic acid may be polymeric.

Examples of polymeric substances bearing a multiplicity of acid groups and which function as oleophilising agents are given in US-A-6 131 514, and in WO 00/37254 and 00/37261.

The acid groups of the oleophilising agents are preferably at least partly neutralised in the form of salts, such as salts of a metal ion such as sodium, potassium and lithium, or ammonium salts including salts of quaternary ammonium compounds, or salts of other cations such as pyridinium.

The anionic oleophilising agent may be present in the aqueous solution or aqueous colloidal dispersion in an amount from 0.02 to 5% by weight, preferably from 0.05 to 1% by weight.

It is necessary that the polymer is in the form of an aqueous solution or a stable colloidal dispersion, so that it can pass through the jets of the

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printer head.

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While water is the preferred aqueous carrier medium, the aqueous composition may comprise one or more water miscible solvents e.g. a polyhydric alcohol such as ethylene glycol, diethylene glycol, triethylene glycol or trimethylol propane. The amount of aqueous carrier medium in the aqueous composition may be in the range from 30 to 99.995, preferably from 50 to 95% by weight.

Jet velocity, separation length of the droplets, drop size and stream stability are greatly affected by the surface tension and the viscosity of the aqueous composition. Inkjet inks suitable for use with inkjet printing systems may have a surface tension in the range from 20 to 60, preferably from 30 to 50 dynes/cm. Control of surface tensions in aqueous inks may be accomplished by additions of small amounts of surfactants. The level of surfactants to be used can be determined through simple trial and error experiments. Anionic and nonionic surfactants may be selected from those disclosed in U.S. Pat. Nos. 5,324, 349; 4,156,616 and 5,279,654 as well as many other surfactants known in the inkjet art. Commercial surfactants include the SURFYNOL<sup>TM</sup> range from Air Products; the ZONYL<sup>TM</sup> range from DuPont; the FLUORAD<sup>TM</sup> range from 3M and the AEROSOL<sup>TM</sup> range from Cyanamid.

The viscosity of the ink is preferably no greater than 20 centipoise e.g. from 1 to 10, preferably from 1 to 5 centipoise at room temperature.

The solution used in the ink jet printer may comprise other ingredients, for instance water-soluble liquids or solids with a substantially higher boiling point than water, e.g. ethanediol. A humectant or co-solvent may be included to help prevent the ink from drying out or crusting in the orifices of the print head. A biocide, such as PROXEL<sup>TM</sup> GXL from Zeneca Colours may be added to prevent unwanted microbial growth which may occur in the ink over time. Additional additives which may be optionally present in the ink include thickeners, pH adjusters, buffers, conductivity enhancing agents, anti-kogation agents, drying agents and defoamers.

The aqueous composition is employed in inkjet printing wherein drops of the composition are applied in a controlled fashion to the surface of the

support by ejecting droplets from a plurality of nozzles or orifices in a print head of an inkjet printer.

Commercially available inkjet printers use several different schemes to control the deposition of the ink droplets. Such schemes are generally of two types: continuous stream and drop-on-demand.

In drop-on-demand systems, a droplet of ink is ejected from an orifice directly to a position on the ink receptive layer by pressure created by, for example, a piezoelectric device, an acoustic device, or a thermal process controlled in accordance with digital signals. An ink droplet is not generated and ejected through the orifices of the print head unless it is needed. Inkjet printing methods and related printers are commercially available and need not be described in detail.

The aqueous composition may have properties compatible with a wide range of ejecting conditions, e.g. driving voltages and pulse widths for thermal inkjet printers, driving frequencies of the piezoelectric element for either a drop-on-demand device or a continuous device, and the shape and size of the nozzle.

After writing the image to the printing plate, the printing plate may be inked with printing ink in the normal way, and the plate used on a printing press. Before inking, the plate may be treated with an aqueous solution of natural gum, such as gum acacia, or of a synthetic gum such as carboxymethyl cellulose, as is well known in the art of printing—see for example Chapter 10 of "The Lithographer's Manual", edited by Charles Shapiro and published by The Graphic Arts Technical Foundation, Inc., Pittsburgh, Pa. (1966).

The invention is further illustrated by way of specific example as follows. Unless otherwise indicated, all percentages are by weight. Example 1

A lithographic substrate according to the invention was prepared by coating polyethylene terephthalate photographic film base from aqueous solution with the following coverages of the stated substances:

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Cationic colloidal silica LUDOX CL TM	$5.0 \text{ g/m}^2$
Polyethyleneimine (used as a 5% w/w solution	
and adjusted to pH 6.5 with sulphuric acid)	$0.8 \text{ g/m}^2$
bis(vinylsulphonyl)methane (hardener)	$0.05 \text{ g/m}^2$

An inkjet writing fluid was prepared as follows:

To 11.5 ml of water was added 2.5 ml of 4% w/w aqueous solution of AEROSOL<sup>TM</sup> 22, 2 ml of ethanediol, and 4 ml of 2% w/w aqueous solution of the dye Phloxine B. (The AEROSOL<sup>TM</sup> 22 was the oleophilising compound of the invention, ethanediol a humectant, and the dye was present to make the fluid visible on the plate).

The black cartridge of a Lexmark Z43 inkjet printer was emptied, the plastic foam removed, and residual ink washed out. It was refilled with the above writing fluid and a wad of cotton wool in place of the foam. The cartridge was replaced in the printer, and a test pattern was printed onto a sheet of the film as described above.

A second test pattern was printed on a sheet of grained and anodised aluminium printing plate substrate which served as a comparative substrate of the prior art.

When the test pattern had dried, the resulting printing plates were mounted on the plate cylinder of a Heidelberg T-Offset printing press, the press rollers were inked up using fount solution (Varn International TM Universal Pink Fount Solution, diluted 1 + 15 with water) and K&E® Novaquick 123W oil-based black ink, and printing started. Clean prints were obtained from the first impression. The quality of the printed impressions of the test pattern was monitored as the print runs continued.

After 500 impressions, it was seen that the prints from the aluminium plate were losing fine detail, and the printing run with that plate was stopped. The prints from the coated film substrate of the invention remained of high quality, and were still of high quality after 2500 impressions, demonstrating the superior press performance of the invention.

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## Example 2

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This example illustrates a substrate of the invention used with writing fluids comprising a variety of oleophilising compounds.

Solutions of the oleophilising compounds were prepared by dissolving them in water at a concentration of 0.5% w/w. If the oleophilising compound was in the form of a free acid, sufficient sodium hydroxide solution was added to convert all the acid to the sodium salt. Each solution was applied to a portion of a hydrophilic substrate with a small squirrel-hair paintbrush, and allowed to dry.

The hydrophilic substrate was a polyethylene terephthalate photographic film base coated from aqueous solution with the following coverages of the stated substances:

٠	Cationic colloidal silica LUDOX CLTM	$3.0 \text{ g/m}^2$
15	Polyethyleneimine (used as a 5% w/w solution	
	and adjusted to pH 6.5 with sulphuric acid)	$0.6 \text{ g/m}^2$
	bis(vinylsulphonyl)methane (hardener)	$0.05 \text{ g/m}^2$

Portions of the hydrophilic substrate were gently wiped with a piece of cotton wool which was wetted with water. A little black lithographic printing ink was then applied to the cotton wool, and the inked cotton wool pad rubbed gently over the substrate. The test was then repeated except the cotton wool was wetted with lithographic press fount solution (Varn International ® Universal Pink Fount Solution, diluted 1 + 15 with water).

This test was carried out with the following compounds according to the invention: AEROSOL<sup>TM</sup> 22, AEROSOL<sup>TM</sup> 18, EMCOL<sup>TM</sup> K8300, and compounds 2, 3, 4, 5, 7, 14, 16, and 18.

AEROSOL<sup>TM</sup> 22 has the structure

$$\begin{array}{c|c} O & CO_2Na \\ H_{37}C_{18} & & SO_3Na \\ \hline & CO_2Na & \\ \hline & CO_2Na & \\ \end{array}$$

AEROSOL<sup>TM</sup> 18 has the structure

EMCOL<sup>TM</sup> K8300, has the structure

Compounds 2 to 5, 7, 14, 16 and 18 have the structures:

Compound 2

Compound 3

Compound 4

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Compound 7

$$Na^{+} - O \longrightarrow O \\ O \longrightarrow NH \\ C_{21}H_{45}$$

Compound 5

Compound 14

$$Na^{+}$$
 O  $NH$  O  $Na^{+}$  O  $Na^{+}$   $C_{15}H_{31}$ 

Compound 16

Compound 18

In the case that the cotton wool was wetted with water and also in the case that the cotton wool was wetted with fount solution, in the area of the substrate to which the solution of each oleophilising compound had been applied, a clear black mark of adhering lithographic ink was observed, while the background areas of the substrate remained unmarked and wetted with water or fount solution. This demonstrated that the compounds showed an oleophilising effect on the substrates used, and so were potentially useful for making lithographic printing plates by inkjet application.

The test was also carried out with the following additional oleophilising compounds:

Sodium dodecyl sulphate,
Sodium benzene dodecyl sulphate,
Tri-isopropyl naphthalene sulphonate,
Dioctyl sulphosuccinate, sodium salt,
Sodium stearate, and

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For all the additional compounds, when the test was done using water as the wetting liquid, in the area of the substrate to which the solution of the compound had been applied, a clear black mark of adhering lithographic ink was

observed, while the background areas of the substrate remained unmarked and wetted with water.

# Example 3

This example illustrates a substrate of the invention used with writing fluids comprising a variety of oleophilising compounds.

The test described in Example 2 was carried out using a number of oleophilising compounds using a hydrophilic substrate which consisted of polyethylene terephthalate photographic film base coated from aqueous solution with the following coverages of the stated substances:

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In addition to the oleophilising compounds used in Example 2, the following compounds were used:

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The resulting mark of adsorbed lithographic printing ink was then subjected to a wet abrasion test to estimate its robustness. A swab of soft cotton fabric was attached to a weight and moved to and fro over the surface, and the number of abrasion strokes required to remove the centre of the mark of adsorbed lithographic printing ink was recorded. The results were as follows:

Compound	Number of
	strokes
2	10
3	2
5	2 .
5	2
7	2
9	28.
11	42
12	37 .
14	50
16 ·	59
18	84

Compounds 2, 9, 11, 12, 14, 16, and 18 were examples of preferred compounds in which the linking group bound to the hydrophobic group is bonded to the carbon atoms between the acid groups via a nitrogen atom, and all showed better abrasion resistance than the substances which did not have that structure. Example 4:

An inkjet writing fluid was prepared as follows:

To 11.5 ml of water was added 2.5 ml of a 4% w/w aqueous solution of AEROSOL<sup>TM</sup> 22, 2 ml of ethanediol, and 4 ml of 2% w/w aqueous solution of the dye Phloxine B. (The AEROSOL<sup>TM</sup> 22 was the oleophilising compound, ethanediol a humectant, and the dye was present to make the fluid visible on the plate).

The black cartridge of a Lexmark Z43 inkjet printer was emptied, the plastic foam removed, and residual ink washed out. It was refilled with the above writing fluid and a wad of cotton wool in place of the foam. The cartridge was replaced in the printer, and a test pattern was printed onto a sheet of the hydrophilic substrate as described in Example 2.

When the test pattern had dried, the resulting polyester film

printing plate was mounted on the plate cylinder of a Heidelberg T-Offset printing press, the press rollers were inked up using fount solution as described in Example 1 and K&E® Novaquick 123W oil-based black ink, and printing started. Clean

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prints were obtained from the first impression, and 2000 copies of the test pattern were printed without noticeable deterioration.

### Example 5

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This example illustrates the substrate of the invention used with a writing fluid which comprises a negatively charged polymer (the anionic polymer AQ55S, a sulphonated polyester, supplied by Eastman Chemical Corporation) in the presence of finely dispersed pigments.

Yellow Pigment Dispersion:

The yellow pigment used in the writing fluid of the present invention was prepared as follows. A mixture was prepared containing the following components: 8000 g of polymeric beads, mean diameter of 50 µm (milling media); 1600 g of Pigment Yellow 155 (Clariant Corp.); 400 g of oleoyl methyl taurine, (OMT), potassium salt and 4880 g of deionized water.

The above components were milled in a 40 liter double walled vessel obtained from BYK-Gardner using a high energy media mill manufactured by Morehouse-Cowles Hochmeyer. The mill was run for approximately 8 hours at room temperature. The dispersion was separated from the milling media by filtering the mill grind through a 4-8 μm KIMAX<sup>TM</sup> Buchner Funnel obtained from VWR Scientific Products. An additional 8000 g of dilution water was added to the filtered dispersion followed by a biocide, PROXEL<sup>TM</sup> GXL (Zeneca Corp.). The pigment is about 9.91% by weight of the total final dispersion and the biocide is about 230ppm by weight of the total final dispersion. The median pigment particle sizes is about 38 nm as measured by MICROTRAC II Ultrafine particle analyzer (UPA) manufactured by Leeds & Northrup.

#### Cyan Pigment Dispersion:

The cyan pigment dispersion was prepared similar to the yellow pigment dispersion except that Pigment Blue 15:3 (Clariant Corp.) was used instead of Pigment Yellow 155. The amount of OMT potassium salt was 25 weight % based on the pigment. The pigment was about 9.97% by weight of the total final dispersion. The median pigment particle size was about 32 nm as measured by MICROTRAC<sup>TM</sup> II Ultrafine particle analyzer (UPA) manufactured by Leeds & Northrup.

Yellow Writing Fluid:

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To prepare the yellow writing fluid, 24.97 g of yellow pigment dispersion described in Example 1 (9.91% active), 0.2 g SURFYNOL<sup>TM</sup> 465 (Air Products Inc.), 8.40 g glycerol, 14.5 g triethylene glycol and 3.00 g di(propyleneglycol) methyl ether (DOWANOL<sup>TM</sup> DPM), and 9.52 g of AQ55<sup>TM</sup> (10.5% active) were added together with distilled water so that the final weight of the ink was 100.0 g. The final ink contained 2.48% Pigment Yellow 155, 0.50% SURFYNOL<sup>TM</sup> 465, 8.40% glycerol, 14.5% triethylene glycol, 3% di(propyleneglycol) methyl ether and 1% AQ55<sup>TM</sup>. The solution was filtered through a 3 μm polytetrafluoroethylene filter.

# Cyan Writing Fluid:

To prepare the cyan writing fluid, 16.55 g of yellow pigment dispersion described in Example 1 (9.97% active), 0.2 g SURFYNOL<sup>TM</sup> 465 (Air Products Inc.), 6.50 g glycerol, 18.7 g triethylene glycol and 3.50 g di(propyleneglycol) methyl ether (DOWANOL<sup>TM</sup> DPM), and 9.52 g of AQ55<sup>TM</sup> (10.5% active) were added together with distilled water so that the final weight of the ink was 100.0 g. The final ink contained 1.65% Pigment Blue 15:3, 0.50% SURFYNOL<sup>TM</sup> 465, 6.50% glycerol, 18.70% triethylene glycol, 3.50% di(propyleneglycol) methyl ether and 1.0% AQ55<sup>TM</sup>. The solution was filtered through a 3 μm polytetrafluoroethylene filter.

The black cartridge of a Lexmark Z43 inkjet printer was emptied, the plastic foam removed, and residual ink washed out. It was refilled in turn with each of the above writing fluids, with a wad of cotton wool in place of the foam. The cartridge was replaced in the printer, and a test pattern was printed onto a sheet of hydrophilic substrate which comprised polyethylene terephthalate photographic film base coated from aqueous solution with the following coverages of the stated substances:

	Cationic colloidal silica LUDOX CL <sup>TM</sup>	$4.0 \text{ g/m}^2$
30	Polyethyleneimine (used as a 5% w/w solution	
	and adjusted to pH 6.5 with sulphuric acid)	$0.4 \text{ g/m}^2$
	bis(vinylsulphonyl)methane (hardener)	$0.024 \text{ g/m}^2$

The resulting imaged printing plates were mounted on a printing press and printed as described in Example 1. Good sharp prints having excellent resolution were obtained for plates made with each of the writing fluids, and 4500 impressions were run without any loss or fading of the test pattern.

#### **CLAIMS**

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- 1. A method for the preparation of a printing plate comprising forming an oleophilic image on a substrate for a printing plate comprising a support having a hydrophilic layer on its surface, the oleophilic image being formed by inkjet printing an aqueous solution or aqueous colloidal dispersion of an anionic oleophilising agent on the surface of the support and drying the applied solution or dispersion, such that on drying the area of the surface to which the solution or dispersion was applied becomes lithographic ink-accepting, characterised in that the hydrophilic layer comprises a crosslinked cationic polymer.
- 2. A method according to claim 1 wherein the substrate is a metallic, polymeric or paper-based support coated with a layer comprising a crosslinked cationic polymer.
- 3. A method according to claim 1 or claim 2 wherein the cationic polymer comprises amino groups selected from primary, secondary, tertiary and quaternary amino groups.
- 4. A method according to any one of the preceding claims wherein the cationic polymer is selected from the group consisting of

  20 polyalkylenepolyamines and alkylated derivatives thereof, products of addition of alkylcarboxylic acids and polyalkylenepolyamines, products of addition of aldehydes and polyalkylenepolyamines, products of addition of aldehydes and polyalkylenepolyamines, products of addition of isocyanates and polyalkylenepolyamines, products of addition of isothiocyanates and polyalkylenepolyamines, products of addition of alkylene oxides and polyalkylenepolyamines and products of addition of polyalkylene oxide block copolymers and polyalkylenepolyamines.
  - 5. A method according to any one of the preceding claims wherein the cationic polymer is polyethyleneimine.
- 6. A method according to any one of the preceding claims wherein the cationic polymer is present in an amount from 0.01 to 10 g/m<sup>2</sup>.

- 7. A method according to any one of the preceding claims wherein the layer comprising a cationic polymer further comprises inorganic particulate material.
- 8. A method according to claim 7 wherein the inorganic particulate material is selected from the group consisting of particulate silica, alumina, titanium dioxide and kaolin.
- 9. A method according to claim 7 or claim 8 wherein the inorganic particulate material is present in an amount from 0.1 to 30 g/m<sup>2</sup>.
- 10. A method according to any one of the preceding claims wherein the anionic oleophilising agent is selected from the group consisting of hydrophobic organic acids and salts thereof.
- 11. A method according to claim 10 wherein the hydrophobic organic acid is selected from hydrophobic organic carboxylates, sulphonates, sulphates, phosphonates and phosphates.
- 12. A method according to claim 11 wherein the hydrophobic organic acid is polymeric.
- 13. A method according to any one of the preceding claims wherein the anionic oleophilising agent is present in the aqueous solution or aqueous colloidal dispersion in an amount from 0.02 to 5% by weight.
- 14. A substrate for a printing plate comprising a support having a hydrophilic layer on its surface wherein the hydrophilic layer comprises a crosslinked cationic polymer.
- 15. A substrate according to claim 14 wherein the support is a metallic, polymeric or paper-based support.
  - 16. A substrate according to claim 14 or claim 15 wherein the cationic polymer comprises amino groups selected from primary, secondary, tertiary and quaternary amino groups.

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- the cationic polymer is selected from the group consisting of polyalkylenepolyamines and alkylated derivatives thereof, products of addition of alkylcarboxylic acids and polyalkylenepolyamines, products of addition of ketones and polyalkylenepolyamines, products of addition of aldehydes and polyalkylenepolyamines, products of addition of isocyanates and polyalkylenepolyamines, products of addition of isothiocyanates and polyalkylenepolyamines, products of addition of alkylene oxides and polyalkylenepolyamines, products of addition of alkylene oxides and polyalkylenepolyamines and products of addition of polyalkylene oxide block copolymers and polyalkylenepolyamines.
  - 18. A substrate according to any one of claims 14 to 17 wherein the cationic polymer is polyethyleneimine.
- 19. A substrate according to any one of claims 14 to 18 wherein the cationic polymer is present in an amount from 0.01 to 10 g/m<sup>2</sup>.
  - 20. A substrate according to any one of claims 14 to 19 wherein the layer comprising a cationic polymer further comprises inorganic particulate material.
- 21. A substrate according to claim 20 wherein the inorganic particulate material is selected from the group consisting of particulate silica, alumina, titanium dioxide and kaolin.
  - 22. A substrate according to claim 20 or claim 21 wherein the inorganic particulate material is present in an amount from 0.1 to 30 g/m<sup>2</sup>.
- 23. A printing plate obtainable by the method according to any one of claims 1 to 13.

# METHOD AND SUBSTRATE FOR THE PREPARATION OF A PRINTING PLATE

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# **ABSTRACT**

A method for the preparation of a printing plate comprises forming an oleophilic image on a substrate for a printing plate comprising a support having a hydrophilic layer on its surface, the oleophilic image being formed by inkjet printing an aqueous solution or aqueous colloidal dispersion of an anionic oleophilising agent on the surface of the support and drying the applied solution or dispersion, such that on drying the area of the surface to which the solution or dispersion was applied becomes lithographic ink-accepting, characterised in that the hydrophilic layer comprises a crosslinked cationic polymer.

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02AUG02 E738135-3 D00113 F01/7700 0.00-02179/9/4

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road Newport Gwent NP9 1RH

Your reference 84218/12403/04 0217979.4 Patent application number (The Patent office will fill in this part) 3. Full name, address and postcode of the or of EASTMAN KODAK COMPANY each applicant (underline all surnames) 343 STATE STREET ROCHESTER **NEW YORK 14650-2201** UNITED STATES OF AMERICA Patents ADP number (if you know it) つりに23090001 If the applicant is a corporate body, give the country/state of its incorporation. **NEW JERSEY** Title of the invention METHOD AND SUBSTRATE FOR THE PREPARATION OF A PRINTING PLATE Name of your agent (if you have one) H HAILE "Address for service" in the United Kingdom KODAK LIMITED to which all correspondence should be sent PATENTS, W92-3A HEADSTONE DRIVE (including the postcode) **HARROW** 08438836001 **MIDDLESEX HA14TY** Patents ADP number (if you know it) 6. If you are declaring priority from one or Priority application number Date of Filing Country (day / month / year) (if you know it) more earlier patent applications, give the country and date of filing of the or of each of these earlier applications and (if you know it) the or each application number Number of earlier application Date of filing If this application is divided or otherwise (day / month / year) derived from an earlier UK application, give the number and the filing date of the earlier application 8. Is a statement of inventorship and of right to grant a patent required in support of this request? (Answer 'Yes' if: YES a) any applicant named in part 3 is not an inventor, or b) there is an inventor who is not named as an applicant, or c) any named applicant is a corporate body. See note (d))

#### Patents Form 1/77

 Enter the number of sheets for any of the following items you are filing with this form.
 Do not count copies of the same document.

Continuation sheets of this form

Description 11

Claim(s)

Abstract

Drawing(s)

10. If you are also filing any of the following, state how many against each item.

**Priority Documents** 

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patent Form 9/77)

Request for substantive examination (Patent Form 10/77)

Any other documents (please specify)

11.

I/We request the grant of a patent on the basis of this application.

A C Haile

Signature

01 Aug 2002

Date

12. Name and daytime telephone number of person to contact in the United Kingdom

H HAILE

020 8424 4419

#### Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- a) If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- b) Write your answers in capital letters using black ink or you may type them.
- c) If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- d) If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- e) Once you have filled in the form you must remember to sign and date it.
- f) For details of the fee and ways to pay please contact the Patent Office.